Fabrication of Ultra Fine Eutectic Structure Using Rapid Quenching Method and Plasma Sintering Technique

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1. Introduction

It is well known that cooling a melt of eutectic composition forms a characteristic structure. In this structure two phases entangles each other, which is called eutectic structure. Such structure is due to an alternate switching of crystallizing components from the melt. The size is generally small (below micrometer). The structure is self-forming composite, which can be used for many composite materials. Kakegawa *et al.* emphasized the effect of diffusion in liquid phase during the formation of eutectic structure. Diffusion and convection of liquid phase delay the switching rate of crystallizing components. Based on this idea, Kakegawa *et al.* used amorphous phase as a mother phase instead of the melt in $GaAlO_3$-Al_2O_3 and YAG-Al_2O_3 system and succeeded to make ultra fine eutectic structures. Eutectic structures having a size of several ten nanometers, which is much smaller than that by the ordinary method, could be obtained by this process

On the other hand, S. Cytron at ARDEC deals with TiB_2-B_4C eutectic system. He realized that the method by K. Kakegawa could be applied to their system. In this co-research Kakegawa is in charge of making an amorphous of this system, and consolidating and crystallizing the amorphous to obtain a material having ultra fine eutectic structure.

2. Results and discussion

2.1 Basic study of eutectic characteristics of the TiB_2-B_4C system

In order to study the basic characteristics of the TiB_2-B_4C system a mixture of TiB_2-and B_4C (TiB_2:B_4C=12:88) was melted. Unfortunately, our laboratory has no furnace that can attain above 2310°C (eutectic point of this system) in an inert atmosphere. Thus we used spark plasma sintering equipment. Graphite punches and sample were electrically insulated from outside graphite die using mica film as shown in Fig. 1. At the center of the sample a pillar of graphite powder compact was placed. Electrical current is concentrated at the graphite pillar, so that it is locally heated. We could attain a temperature above 2310°C around there. The sample around the graphite pillar was melted. SEM image of a polished section of the melted sample is shown in Fig.

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14. ABSTRACT

It is well known that cooling a melt of eutectic composition forms a characteristic structure. In this structure two phases entangles each other, which is called eutectic structure. Such structure is due to an alternate switching of crystallizing components from the melt. The size is generally small (below micrometer). The structure is self-forming composite, which can be used for many composite materials. Kakegawa et al. emphasized the effect of diffusion in liquid phase during the formation of eutectic structure. Diffusion and convection of liquid phase delay the switching rate of crystallizing components. Based on this idea, Kakegawa et al. used amorphous phase as a mother phase instead of the melt in GaAlO3-Al2O3 and YAG-Al2O3 system and succeeded to make ultra fine eutectic structures. Eutectic structures having a size of several ten nanometers, which is much smaller than that by the ordinary method, could be obtained by this process.

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2. Eutectic structure was not observed. One reason may be the unbalanced volume ratio of TiB_2:B_4C (about 1:11). Eutectic systems having such volume unbalance does not tend to form the typical eutectic structure. The composition used here was chosen according to "Phase diagrams for Ceramists" issued by the American Ceramic Society. Another possible reason may be that the eutectic composition was not correct. We are planning to do with another composition.

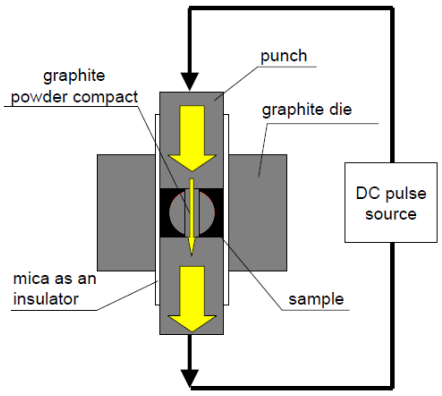

Fig. 1 Assembly to melt the sample

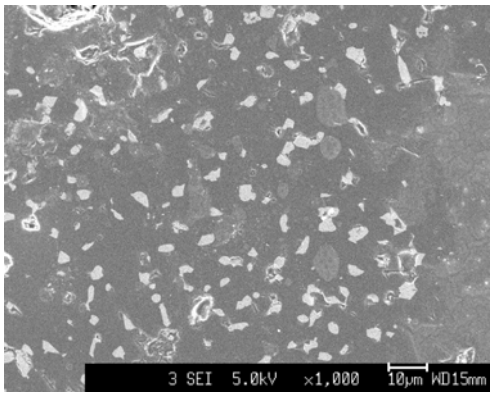

Fig. 2 SEM image of the sample melted by SPS appratus

As a next step we employed YAG laser. YAG laser generates very high temperature at a very small area. By this melting the cooling rate is very high because the volume of the melted part is very small and the melted part is surrounded by solid sample. Thus this can be used for a preliminary experiment of rapid quenching.

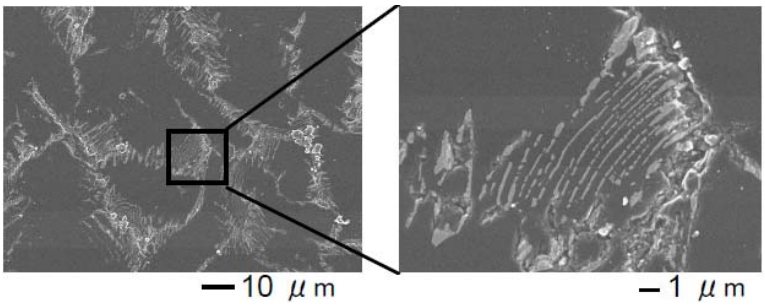

Fig. 3 SEM patterns of the part of the sample, which was exposed to a YAG laser ray. (TiB_2:B_4C = 12:88)

Figure 3 shows SEM pattern of a polished section of the melted part of the sample by YAG laser. The molar ratio of TiB_2:B_4C is 12:88. Eutectic structure was observed partly. Considering the fact that slow cooling of the same composition did not result in the

eutectic structure, quick cooling is important for the formation of eutectic structure in this system. In this experiment we tried another composition, TiB_2:B_4C =25:75. The SEM image of a polished section of this composition is shown in Fig. 4. Eutectic structure was observed over the entire surface. We need to compare with a microstructure of a slow cooled material at this composition.

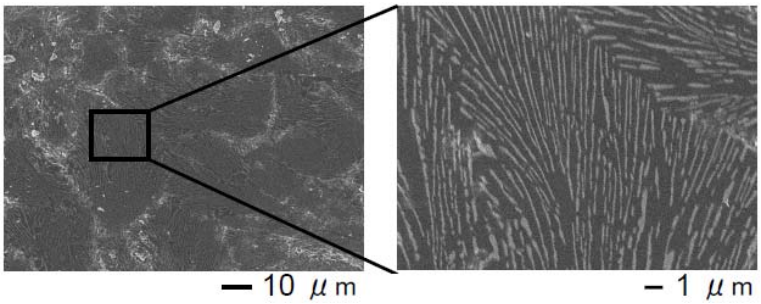

Fig. 4 SEM patterns of the part of the sample, which was exposed to a YAG laser ray. (TiB_2:B_4C = 25:75)

2.2 Attempt for obtaining amorphous material in the TiB_2-B_4C system

One end of a rod-shaped sintered body of TiB_2-B_4C system (TiB_2-B_4C =25:75 in molar ratio) was put into a flame of an arc discharge. The equipment was put in an acrylic resin case, and argon gas was flown. In argon gas environment large flame of the arc discharge could not be possible. When the distance of the carbon electrodes was increased, the flame vanished. The longest distance of the carbon electrodes was shorter than the thickness of the rod-shaped sample (4.6 mm in thickness).

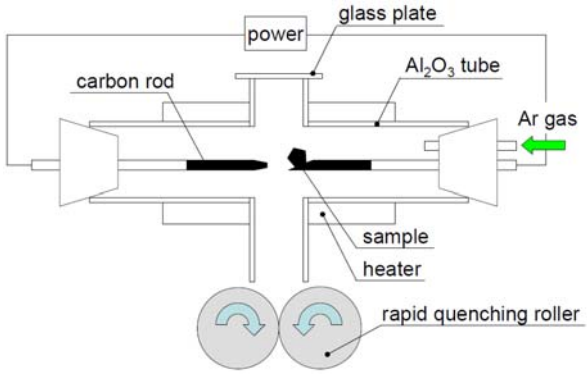

Fig. 5 Apparatus of rapid quenching system with heater

In order to put the sample in the shrunken flame of the arc discharge, sample was crushed into a small piece (about 1 mm). The end of the one carbon electrode was formed as a spatula shape. The small piece of the sample was put on it and the arc discharge

was generated. However it did not melt. The reason was the high melting point (2310°C) of the sample and lowered temperature of the flame due to the argon atmosphere.

Then we tried to bias the temperature of the flame. Figure 5 shows the apparatus of the rapid quenching system with heater. In order to make argon atmosphere the carbon electrodes were put in an alumina tube. Argon gas was flown from one side of the alumina tube. The temperature of the heater was about 500°C. The sample still did not melt.

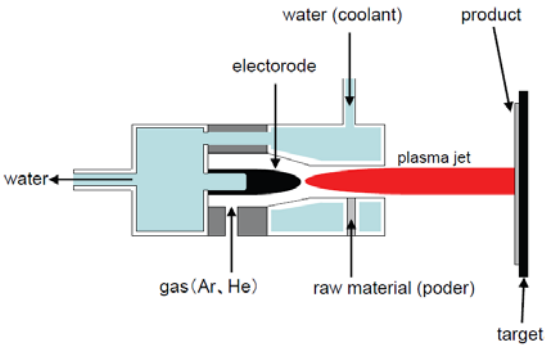

Fig. 6 Scheme of plasma spray

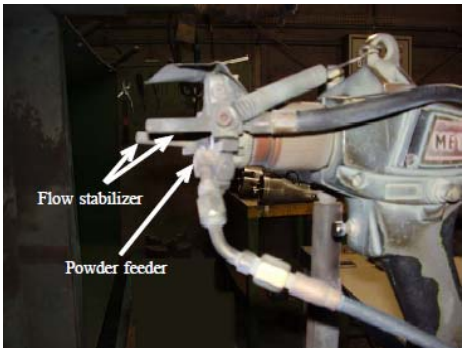

Fig. 7 Plasma spray gun

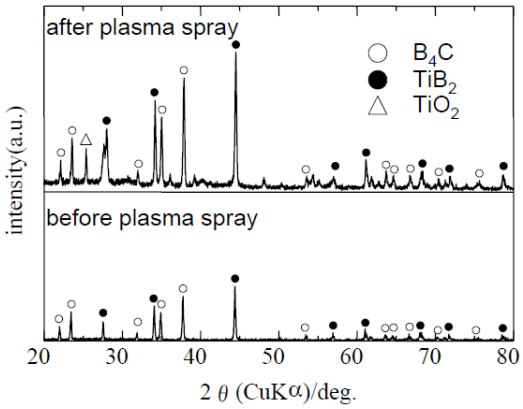

Fig. 8 XRD patterns of the samples before and after the plasma spray

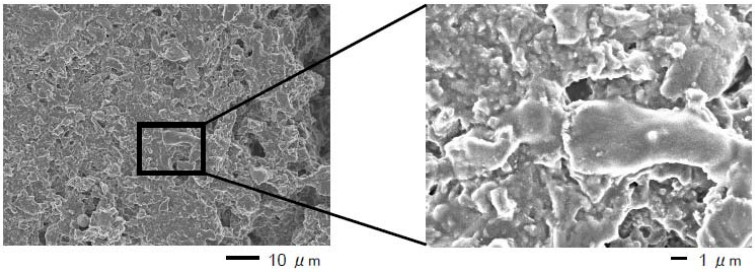

Fig. 9 Cross section of the plasma sprayed sample

Plasma spray method is a candidate to melt materials having high melting point. It attains 5000-6000°C. It is much higher than that attained by oxygen-acetylene burner. The scheme of the plasma spray is illustrated in Fig. 6. It has a flow stabilizer as shown in Fig. 7. An air flow from it stabilizes the shape of the plasma jet. In the case that TiB_2-B_4C system is plasma sprayed the sample tends to be oxidized. As a first step of the plasma spray experiment the air of the flow stabilizer was stopped. It was sprayed against a stainless steel (50 mm × 50 mm in width and 10 mm in thickness). Black granules were deposited on the stainless steel. The sample was successfully melted. XRD pattern of this sample is shown in Fig. 8. XRD pattern before the plasma spray is also shown. Peaks of TiO_2 were observed after the plasma spray. A part of the sample was oxidized. Compared with the strength of the main peak of TiB_2, the amount of the oxidized part does not seem to be serious. We are planning to equip an additional flow stabilizer with an argon gas flow. In addition to this we are also planning to spray the sample into water. In the case of spraying onto the stainless steel, the deposited sample was heated by the successive heat by the spray flame. This seems to oxidize the sample which has already deposited. Spraying into water can avoid such heating. This may result in a formation of amorphous.

Figure 9 shows SEM images with two kinds of magnification for the sample (TiB_2:B_4C = 12:88) deposited on the stainless steel by the plasma spray. Although the sample was not amorphous, distinguishable two phases were not observed. This means that the microstructure is very fine. Even if amorphous cannot be obtained, ultra fine eutectic structure is expected.

3. Future work

Melting of TiB_2-B_4C system in an inert atmosphere had been very difficult. Now we have succeeded to melt it by a use of plasma spray method. Improvement of this is as follows;

[1] Development of an attachment of the flow stabilizer with an argon gas.

[2] Spraying into water, in order to quench the molten sample.

After the experimental of the plasma spray, it will be consolidated using spark plasma sintering equipment.

Plasma spray is conducted in a company with a rental fee. Rental fee is needed every time. The company locates in Nagoya area far from Tokyo area where Chiba University locates. The researcher needs to travel there many times. Modifications of the equipments are needed. This work needs continuous financial support.

In this point many barriers for the preparation of consolidated material having ultra

fine eutectic structure have been crossed. Next stage will accomplish the purpose.